

Advanced Electronic Tongue Concept¹

Martin G. Buehler, Jet Propulsion Laboratory, California Institute of Technology, martin.g.buehler@jpl.nasa.gov

Didier Keymeulen, Jet Propulsion Laboratory, California Institute of Technology, didier.keymeulen@jpl.nasa.gov

Samuel P. Kounaves, Department of Chemistry, Tufts University, samuel.kounaves@tufts.edu

Gregory M. Kuhlman, Jet Propulsion Laboratory, California Institute of Technology, gregory.m.kuhlman@jpl.nasa.gov

Abstract—This effort is directed at developing a sensor for evaluating water quality. It is based on electrochemical techniques to detect and identify ions in solution. This paper discusses the use of Cyclic Voltammetry (CV), corrosion measurements, and Anodic Stripping Voltammetry (ASV) to measure four marker ions Cu, Ni, Fe, and Zn using Electronic Tongue 1. Use of genetic algorithms are suggested as an approach to facilitate the search for optimum measurement conditions. In addition, the possibility of changing the physical conditions of the sample chamber is discussed as a way of increasing the sensor's apparent sensitivity and increasing confidence in the measurement results.

TABLE OF CONTENTS

1. INTRODUCTION
2. EXPERIMENTAL APPARATUS
3. ELECTRONICS
4. EXPERIMENTAL RESULTS
5. SENSOR CONTROL AND PATTERN MATCHING
6. CONCLUSION
7. REFERENCES
8. ACKNOWLEDGEMENTS
9. BIOGRAPHIES

1. INTRODUCTION

This paper extends the work reported at last years IEEE Aerospace conference where the design principles were discussed for the fabrication of Etng1 (Electronic Tongue No. 1) [Buehler, 2001]. In this effort the capabilities of Etng1 are explored using three sets of electrochemical measurements including Cyclic Voltammetry (CV) [Kissinger, 1996], corrosion measurements [Stansbury, 2000], and Anodic Stripping Voltammetry (ASV) [Wang, 2000]. This effort is an outgrowth of the 25-cm³ electrochemical cell developed for the MECA (Mars Environmental Compatibility Assessment) project [West, 1999] which included 20 prefabricated Ion Selective Electrodes, a conductivity sensor, a temperature sensor and a oxidation reduction potential sensor.

This is a joint effort between JPL, Tufts University, and Orion Research, Inc. Its goal is the development of a water quality sensor for use on the International Space Station Alpha and Martian Habitats. The target ions are K⁺ (340 mg/L), Ca²⁺ (30 mg/L), Mg²⁺ (50 mg/L) and Cl⁻ (200 mg/L) which represent some of the NASA Spacecraft Maximum Contaminant Levels (MCL) for potable water for International Space Station Alpha.

2. EXPERIMENTAL APPARATUS

The working electrodes (WE) and reference electrodes (RE) used in this effort were fabricated on ceramic substrates as seen in Fig. 1.

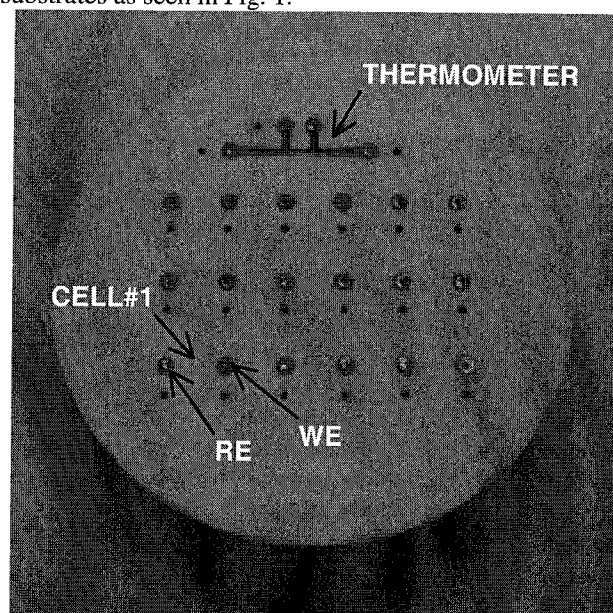


Figure 1. Top side of a 4.5-cm diameter ceramic substrate showing the working (WE) and reference (RE) electrodes arranged on a 3 × 3 array and a four-terminal thermometer.

The electrodes are arrayed in a 3 × 3 matrix with WE and RE. The thermometer is formed by screen printing RuO₂ and is used to monitor the temperature of the solution. The

¹ 0-7803-6599-2/01/\$10.00 © 2001 IEEE

WE and RE Pd(12%)Ag(88%) electrodes were screened printed onto the 1-mm thick 96% pure alumina substrate and fired in air at 840°C. The electrodes are accessed using 0.5-mm diameter pins mounted on the underside of the substrate.

The substrate is mounted in the apparatus shown in Fig. 2a. The top of the chamber contains an array of nine Au/Ni plated Cu auxiliary electrodes (AE) located above the WEs. The distance between the WE and AE is about 2 mm. The volume of the chamber is about 1.5 mL.

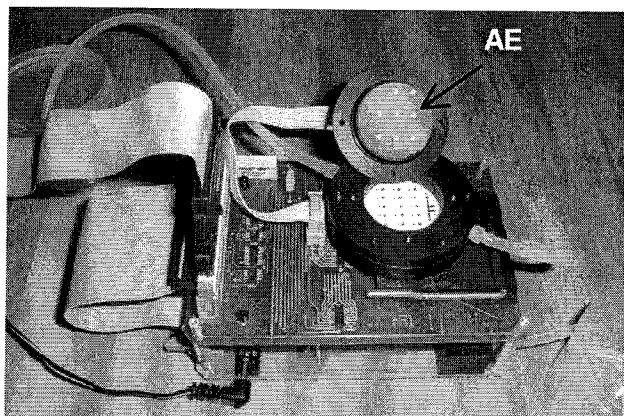


Figure 2a. Etng1 experimental apparatus showing the sample chamber exposed and the nine AEs located in the cap of the chamber.

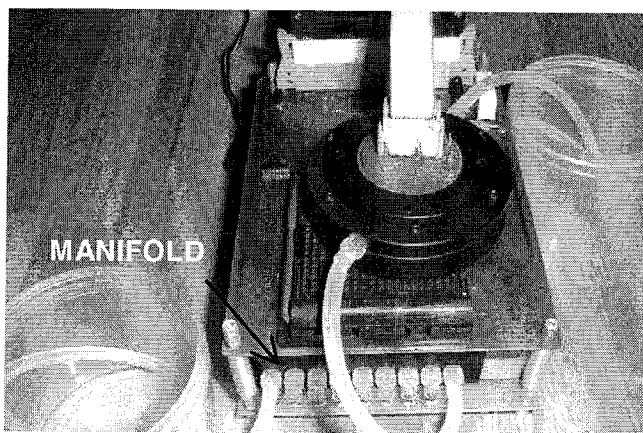


Figure 2b. Etng1 showing the eight-port manifold mounted on the lower fluidics board.

A further view of the apparatus is seen in Fig. 2b that shows the sample chamber mounted on an electronics board which is mounted above a fluidics board that includes an eight-port manifold. Thus, eight reagents can be introduced into the chamber either one at a time or in mixtures by controlling the valves (not shown) above the manifold.

The final view of the apparatus, shown in Fig. 2c, depicts the miniature 50- μ L pump. The pump is operated at 3 Hz and so is capable of filling the 1.5 mL chamber in 10 s.

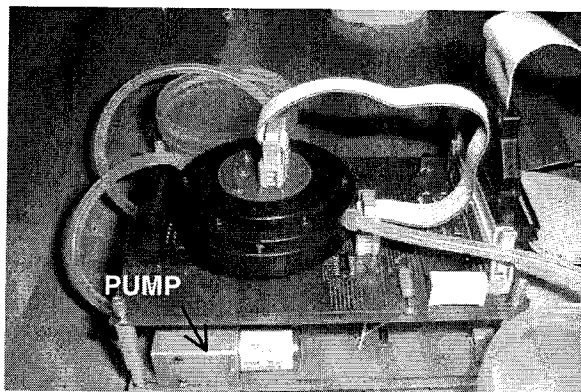


Figure 2c. Etng1 showing the 50- μ L pump mounted on the lower fluidics board.

3. ELECTRONICS

Various solutions were measured using the three-electrode potentiostat shown in Fig. 3 [Kissinger, 1996]. The electronics forces a voltage between the WE and RE to be at voltage determined by DAC0. This is achieved using the operational amplifier U2 to force a current through AE so that the commanded voltage between the WE and RE is achieved. The current through the addressed cell is determined from the voltage drop across R0. The main current flow is indicated for Cell#2 by the red (heavy) line in Fig. 3. The voltage between WE and RE is noted as VWR and the voltage between the AE and RE is noted as VAR.

4. EXPERIMENTAL RESULTS

The apparatus was exercised using four 0.1% by weight salt solutions of CuSO₄, NiSO₄, Fe₂SO₄, and ZnSO₄. Prior to exposure to these salts, the chamber was filled with deionized water. During this exposure, water creates a thin AgO₂ layer on the PdAg WE. The solutions were characterized using CV measurements with a triangle wave voltage with a slope of 0.1 V/s. One hundred stepped voltages formed the triangle wave that varied from +1.0 V to -1.2 V and back to +1.0 V. Two cycles were measured to demonstrate repeatability. Then fifty stepped ASV measurements were taken after a deposition time of T_{dep} with a slope of 0.1 V/s where the linear ramp was varied from -1.2 V to +1.0 V. Again two traces were measured to demonstrate repeatability.

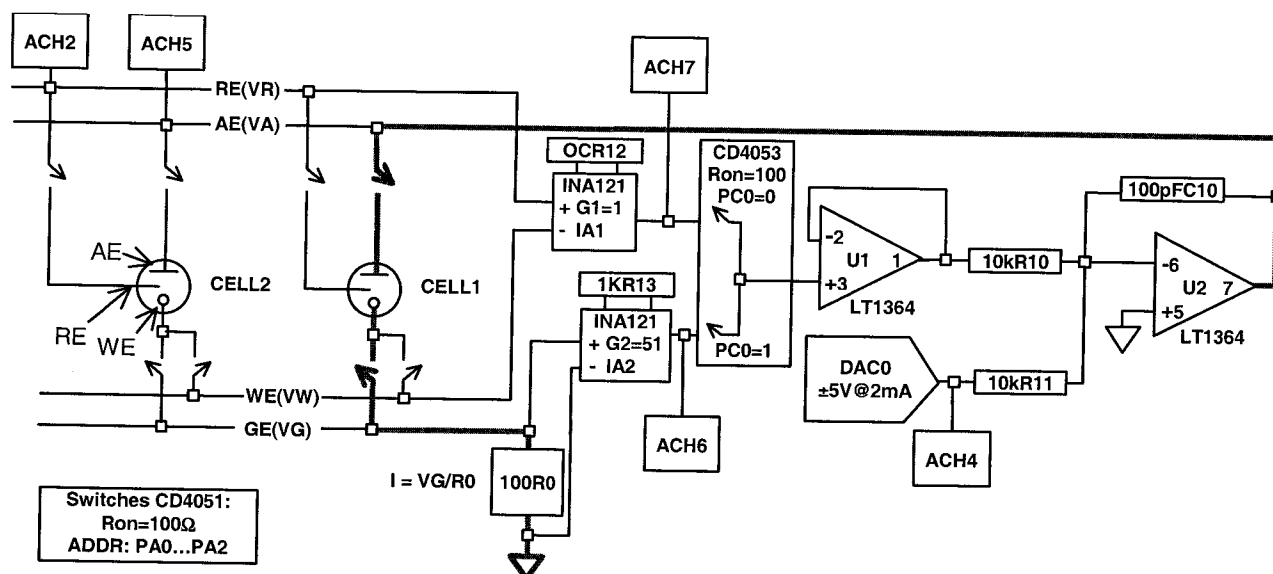


Figure 3. Etng1 potentiostat circuitry. Resistor values are in ohms. ACH and DAC points go to NI DAQcard-1200.

The CV test results are shown in Fig.4. The open data (red curve) are VWR results and the solid data (blue curve) are VAR results. The CV curves provide insight into the nature of the chemical and electrochemical process occurring in the chamber [Kissinger, 1996]. During the negative going sweep (left to right) species in solution are reduced. During the positive going sweep (right to left) species in solution are oxidized. Species identification, however, is determined in subsequent analyses, in particular with ASV.

The CV data reported in Fig. 4 are replotted as Evans curves in Fig. 5. The open data (red curves) are oxidation results measured at the WE and the solid data (blue curve) are reduction results measured at the AE. In the analysis of this corrosion data the intersection of the two curves defines the corrosion potential, E_{corr} , and the corrosion current, I_{corr} [Stansbury, 2000].

ASV measurements shown in Fig. 6 identify the metals in solution. These measurements start at a negative potential of VWR = -1.2 V where they are held for a deposition time, T_{dep} and terminate at 1.0 V. The curves shown in Fig. 6 have negative going peaks characteristic of the ions being measured except for Ni. For the case of Ni, the electroplating literature indicates that no peak should appear for Ni does not exist as a simple ion in solution but is complexed. In this study our goal was to detect marker ions in solution in order to characterize the response of the quasi Ag RE. The ultimate goal is to use the ASV technique to detect very low levels (ppb [Wang2000]) of contaminants in water.

The results of this investigation are summarized in Fig. 7 where the measured results are plotted against the SHE (Standard Hydrogen Electrode) voltages. The ASV results

from Fig. 6 are shown as the triangle data and are compared to the Tufts [Kounaves, 2001] results shown by the diamond data. The difference between the two data sets is attributed to differences in the reference electrodes and differences in the exciting signal. The Tufts results were measured using a Ag/AgCl RE and a square wave exciting signal; whereas, the results from this investigation used a quasi Ag RE and a step exciting signal.

Also shown in Fig. 7 are results taken from the Evans curves shown in Fig. 5. These results indicate a weaker dependence on the SHE. It is noted that the Ni peak does not appear in the ASV data but can be plotted as seen in the figure.

These measurements have a large parameter space. For instance, the exciting signals have a span (1.0 to -1.2 V), a sweep rate (0.1 V/s), waveform (step versus pulse) and deposition time. Likewise, the measured signals have a span and gain. The measurement conditions vary depending on the ion in solution and its concentration. In addition the chamber environment can be altered by changing temperature, adding oxygen or nitrogen, or by changing pH or adding complexing agents. Finally, the condition of the electrode surfaces, which can change with use, also influences the measurements. All of these factors contribute to the multi-parameter measurement space. For these reasons, the use of computer searching techniques is seen as essential to speeding progress during the development cycle, facilitating the search for optimum measurement conditions and increasing the apparent sensitivity and confidence in the measurements.

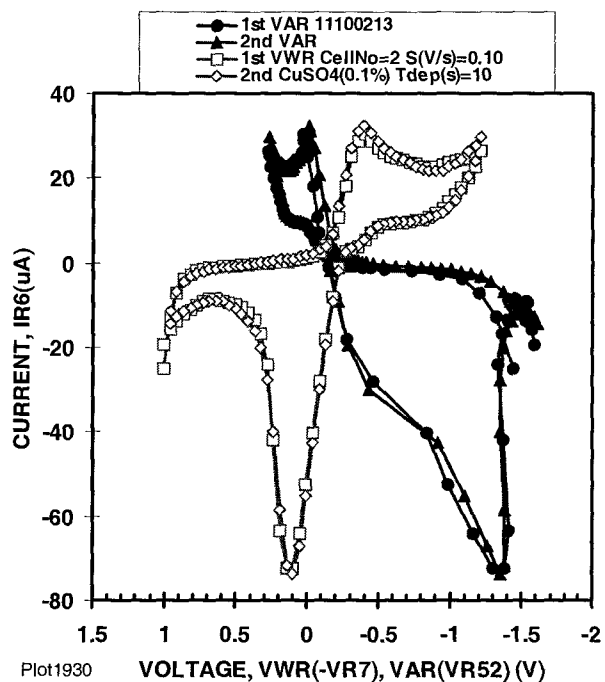


Figure 4a. CV CuSO₄ response for PdAg WE and RE.

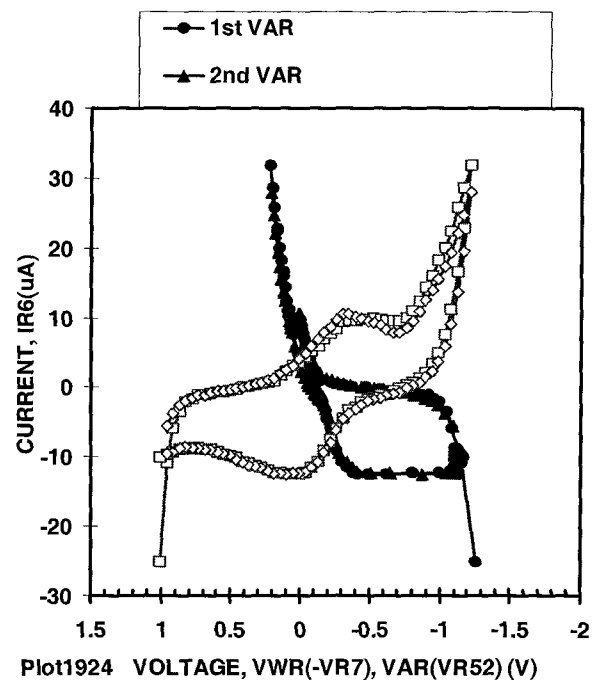


Figure 4c. CV Fe₂SO₄ response for PdAg WE and RE.

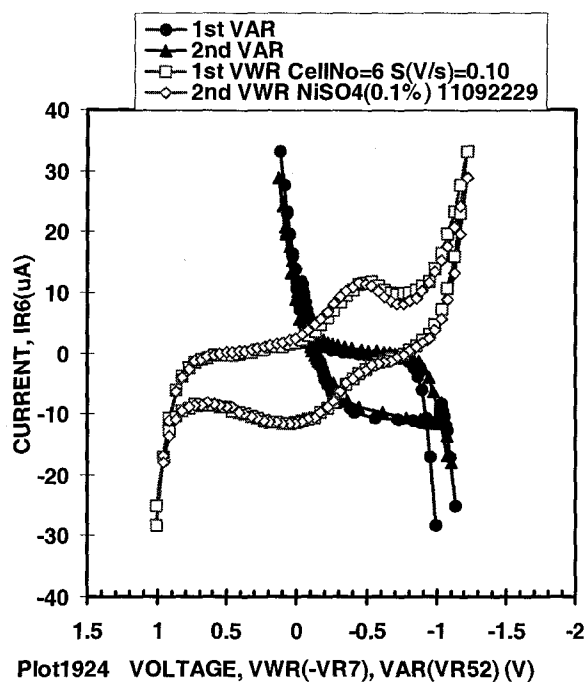


Figure 4b. CV NiSO₄ response for PdAg WE and RE.

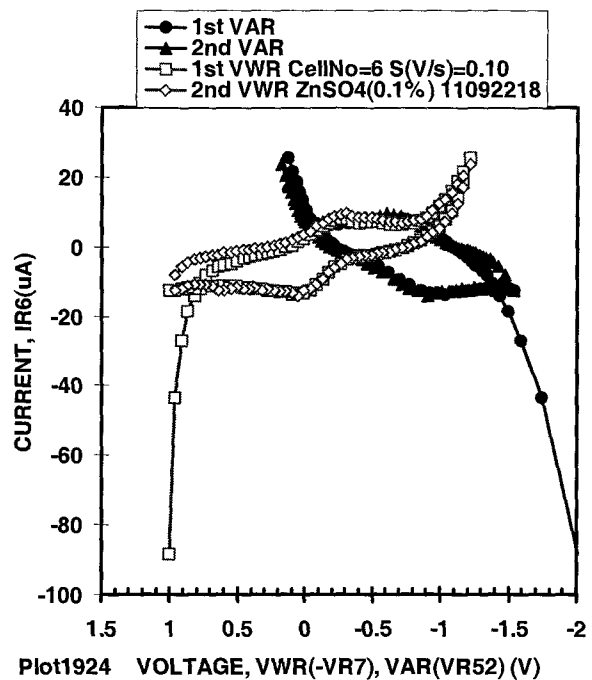


Figure 4d. CV ZnSO₄ response for PdAg WE and RE.

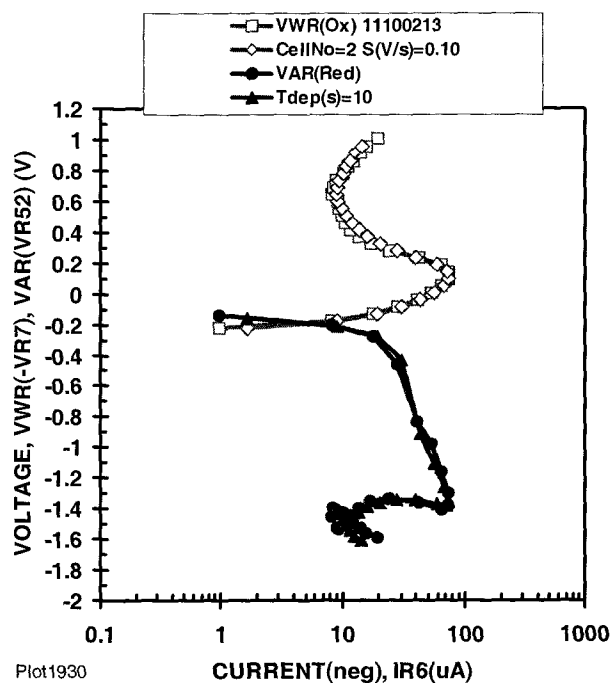


Figure 5a. Evans CuSO₄ response for PdAg WE and RE and Au AE.

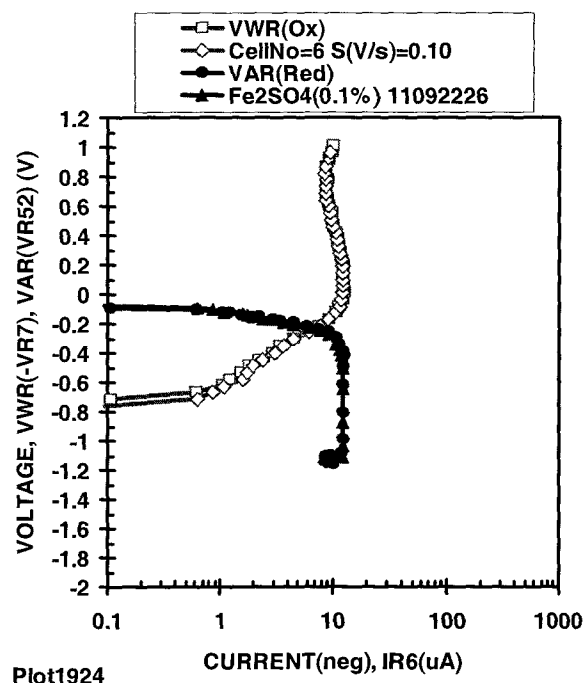


Figure 5c. Evans Fe₂SO₄ response for PdAg WE and RE and Au AE.

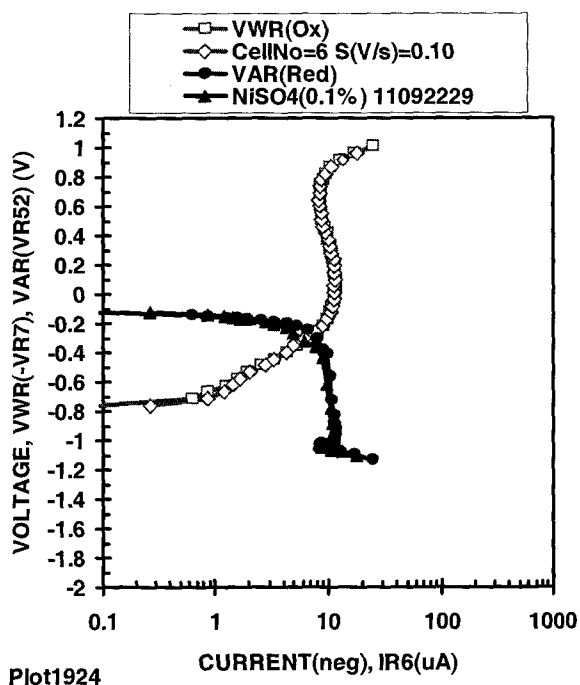


Figure 5b. Evans NiSO₄ response for PdAg WE and RE and Au AE.

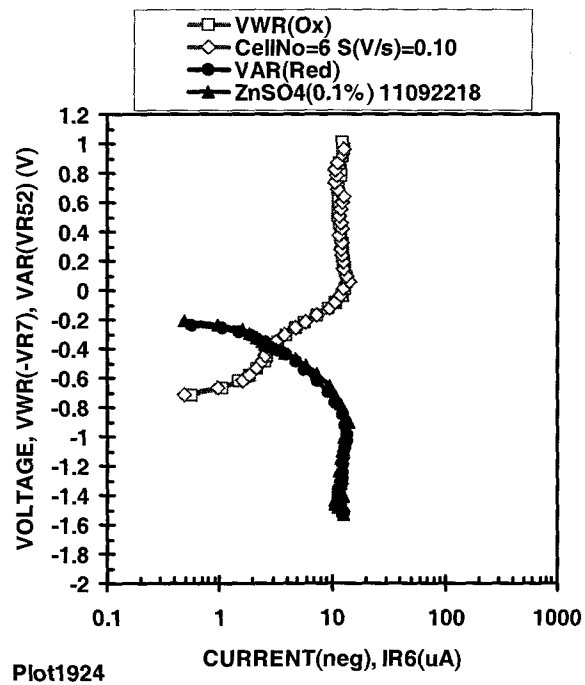


Figure 5d. Evans ZnSO₄ response for PdAg WE and RE and Au AE.

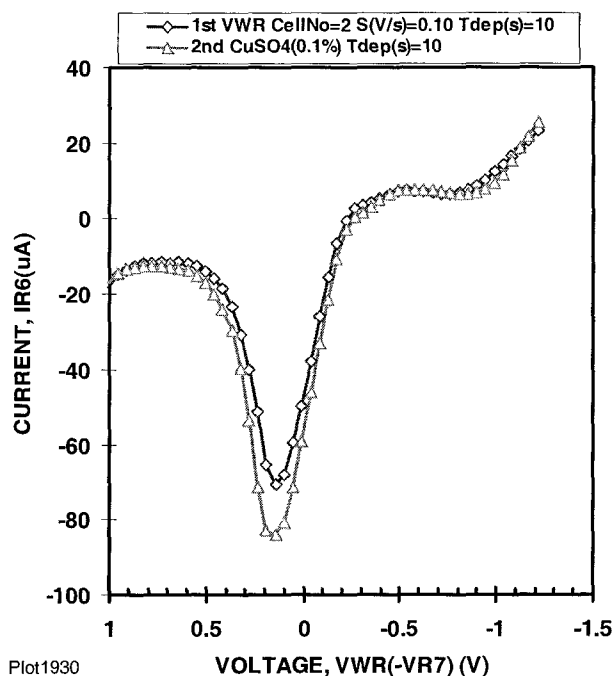


Figure 6a. ASV CuSO₄ response at a PdAg WE for T_{dep}(s) = 10. A negative going peak occurs at VWR = 0.15V.

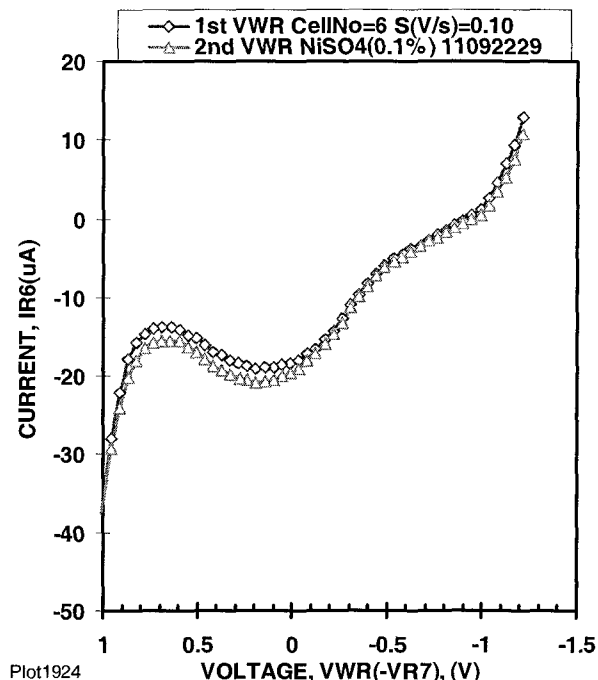


Figure 6c. ASV NiSO₄ response at a PdAg WE for T_{dep}(s) = 50. No Ni peak is visible in this data set.

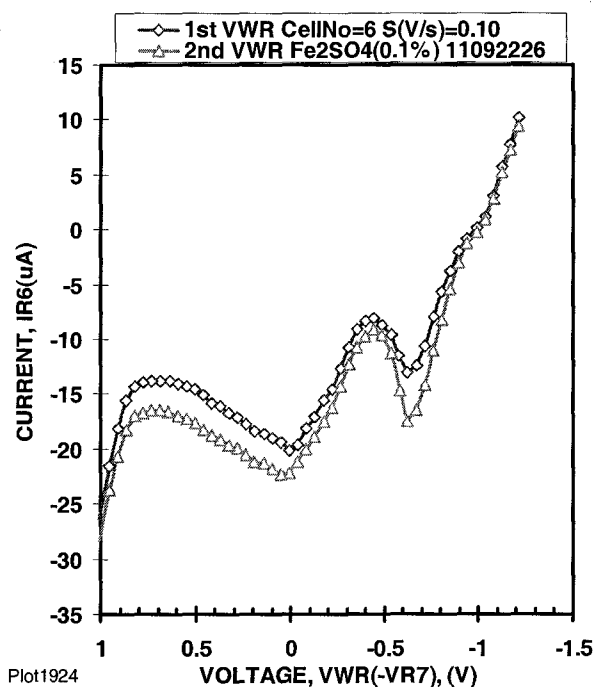


Figure 6b. ASV Fe₂SO₄ response at a PdAg WE for T_{dep}(s) = 50. A negative going peak occurs at VWR = -0.61V.

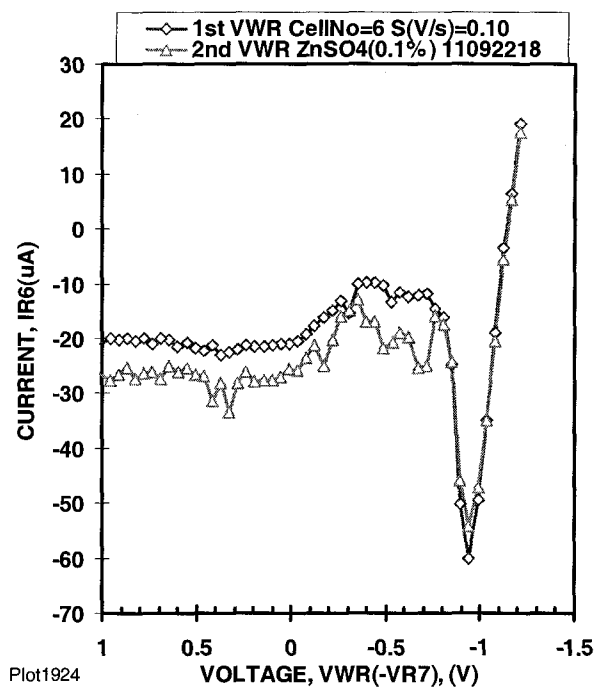


Figure 6d. ASV ZnSO₄ response at a PdAg WE for T_{dep}(s) = 50. A negative going peak occurs at VWR = -0.95V.

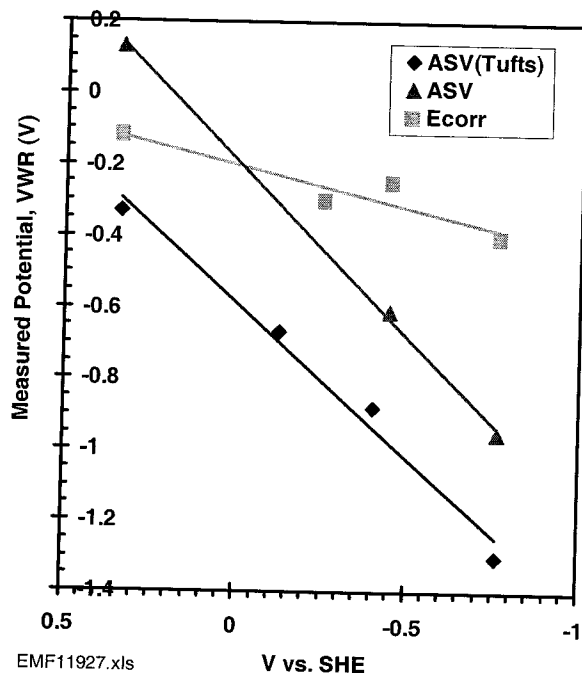


Figure 7. Response of Etng1 ASV peaks and Ecorr versus the SHE (standard hydrogen electrode) potential. Also shown are the ASV peaks reported by Tufts [Kounaves, 2001].

5. SENSOR CONTROL AND PATTERN MATCHING

The approach to detecting contaminants in water is depicted in Figure 8. It is based on a Genetic Algorithm (GA) that has two purposes: (1) to optimize the pattern matching algorithm based on chemometric techniques and the immune system and (2) to design and select the optimal experimental parameters that control the conditions in the sample chamber. The genetic algorithm is used because it is useful in high-dimensional search spaces and makes less assumptions about the search space than strong optimization method like gradient search. GAs use concepts gleaned from Darwin's theory of evolution by natural selection and also from the mechanisms involved in the alteration and transfer of genetic information to individuals in a population [Goldberg, 1989]. GA has been used by the Evolvable Hardware group at JPL for on-chip analog circuit optimization [Stoica, 2001], self-repaired circuit [Keymeulen, 2000] and optimal in-situ signal conditioning [Keymeulen, 2001].

Consider our immune system as functioning like a pattern recognition mechanism and the genetic algorithm as an investigation mechanism to search for impurities in water. Our immune system protects us from an extraordinary large variety of bacteria, viruses, and other pathogenic organisms. It also constantly surveys the body for the

presence of abnormal cells, such as tumor cells and virally infected cells and destroys such cells when they are found. To perform these tasks the immune system must be capable of distinguishing good cells and molecules, which it should not be destroyed, from foreign cells and molecules (antigens), which should be destroyed. From an information-processing perspective, recognizing an almost limitless number of foreign cells and molecules, and distinguishing these from the good ones is a formidable task.

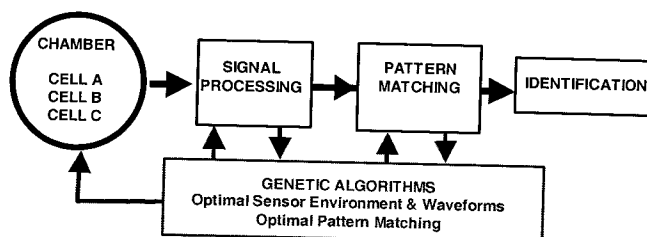


Figure 8. Sensor control and pattern matching using genetic algorithm.

In this effort models will mimic the pattern recognition process and learning that takes place in the immune system. Models have been developed and applied to the detection of computer viruses [Forrest, 1997] and novelty detection in time series data [Dasgupta, 1999]. There the virus must be detected and patterns recognized in unknown computer environments. We will apply the same strategy, as well as chemometric techniques, in our system to learn the signatures of known impurities in water and be able to differentiate from unknown impurities.

The genetic algorithm is also used to determine the optimal parameters that control the conditions found in the sample chamber. That is, after the initial signals are detected from the sample chamber, the results are analyzed by looking for matching patterns. The adaptive control then searches using a genetic algorithm for suggestions on how to modify the environment of the sample chamber or how to alter the signals used to measure the sensor. For example, the sample chamber environment can be altered by changing the temperature, altering the pH, or adding complexing reagents. The sensor waveform signals can be altered by changing the signal gain or by altering the parameters that determine the square-wave sweep parameters. Thus, the first answer can be refined to provide a more informed second answer. In this way we hope to be able to discriminate between contaminants in the water and increase the apparent sensitivity of the sensors.

6. CONCLUSION

This paper presented CV, Corrosion and ASV results from Etng1 using four marker ions: Cu, NI, Fe, and Zn. The results illustrate the complexity of measurement conditions that involve: (a) exciting signal, (b) measured signal, (c) chamber environment, and (d) ion detected. The use of genetic algorithm is seen as essential to speeding progress during the development cycle, facilitating the search for optimum measurement conditions and increasing the apparent sensitivity and confidence in the measurements.

7. REFERENCES

- M. G. Buehler, S. P. Kounaves, D. P. Martin, S. J. West, G. M. Kuhlman, "Designing a Water-Quality Monitor Using an Array of Ion Selective Electrodes, Proceedings of the IEEE Aerospace Conference, (March 2001).
- D. Dagupta and S. Forrest. Artificial Immune Systems in Industrial Applications. In *Proc. of the Int Conf on Intelligent Processing and Manufacturing Material*. Honolulu, HI, July 10-14, 1999.
- S. Forrest et al. Computer Immunology. In *Communications of the ACM* Vol. 40, No. 10, pp. 88-96 (1997).
- D. E. Goldberg. *Genetic Algorithms in Search, optimization and Machine Learning*, Addison-wesley: Reading, MA, 1989.
- D. Keymeulen, A. Stoica, R. Zebulum. Fault-Tolerant Evolvable Hardware using Field Programmable Transistor Arrays. In *IEEE Trans. on Reliability, Special Issue on Fault-Tolerant VLSI Systems*, vol. 49, No. 2, 2000. IEEE Press.
- D. Keymeulen, R. Zebulum, A. Stoica, M. Buehler. Initial Experiments of Reconfigurable Sensor Adapted by Evolution. In *Proc. of Int Conf on Evolvable Systems*, October 3-5, 2001, Tokyo, Japan. Springer-Verlag.
- P. T. Kissinger and W. R. Heineman, *Laboratory Techniques in Electroanalytical Chemical*, Marcel Dekker (New York, 1996).
- S. P. Kounaves, Tufts University, private communication, 2001.
- E. E. Stansbury and R. A. Buchanan, *Fundamentals of Electrochemical Corrosion*, ASM Int. (Materials Park, OH, 2000).

J. Wang, *Analytical Chemistry*, Wiley-Vch, New York, 2000.

S. J. West, X. Wen, R. Geis, J. Herdan, T. Gillette, M. H. Hecht, W. Schubert, S. Grannan, S. P. Kounaves, "Electrochemistry on Mars," *American Laboratory* 31 (20), p. 48-, Oct. 1999

8. ACKNOWLEDGMENTS

The work described in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. The overall effort is supported by a grant from the National Aeronautics and Space Administration under the Advanced Environmental Monitoring and Control Program. The authors are indebted to our program manager, Darrell Jan, for his support.
File: EtngAero1A18.doc.

9. BIOGRAPHIES



Martin G. Buehler received the BSEE and MSEE from Duke University in 1961 and 1963, respectively and the Ph.D. in EE from Stanford University in 1966 specializing in Solid State Electronics.

He worked at Texas Instruments for six years, at National Bureau of Standards (now NIST) for eight years, and since 1981 has been at the Jet Propulsion Laboratory where he is a senior research scientist. At JPL he has developed p-FET radiation monitors for CRRES, Clementine, TELSTAR and STRV, E-nose which flew on STS-95, and an electrometer for the Mars '01 robot arm. Currently he serves on the staff of the New Millennium Program as a technical analyst. Martin is a member of the IEEE, Tau Beta Pi, and Sigma Nu. He holds 12 patents and has published over one hundred papers.

Didier Keymeulen received the BSEE degree from the Universite Libre de Bruxelles, Belgium, in 1987 and the MSEE and Ph.D. in Electrical Engineering and Computer Science from the Vrije Universiteit Brussels, Belgium in 1991 and 1994, respectively with the specialization in Artificial Intelligence. In 1995 he was the Belgium laureate of the Japan Society for the Promotion of Science Post Doctoral Fellowship for Foreign Researchers. In 1996 he joined the computer science division of the Japanese

National Electrotechnical Laboratory as senior researcher. Since 1998, he is member of the technical staff of JPL in the Advanced Computing Technologies Group. At JPL, he is responsible for the applications of the DARPA project on evolvable hardware for adaptive computing that leads to the development of fault-tolerant electronics and autonomous and adaptive sensor technology. His expertise is in adaptive and learning hardware for autonomous systems. He is the author of over 30 papers covering topics in qualitative modeling for diagnostic and control of physical systems, adaptive and learning systems for mobile robot navigation and implementation of dynamical systems on massively parallel computers. He served as the co-chair of the NASA/DoD Workshop on Evolvable Hardware and served as its co-chair in 1999, program co-chair in 2000, and chairman in 2001. Didier is a member of the IEEE.

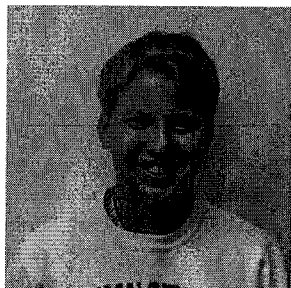
Samuel P. Kounaves received his BS/MS from Cal State - San Diego in 1976/78 and his Ph.D. (D.Sc.) from the



University of Geneva in Switzerland in 1985. After a post-doctoral fellowships at SUNY-Buffalo and Harvard University he joined the faculty at Tufts University in 1988, where he is currently an Associate Professor of Chemistry. He has an active research group of 8 Ph.D. students and one undergraduate. He has been a

principal investigator on more than 15 grants from government (NSF, EPA, DOE) and industry (PRF, EG&G, Orion). He has authored over 50 publications and holds 3 Patents. His research has been directed at the development of microfabricated electrochemical and chemically modified sensors, for use in monitoring and investigation of remote hostile environments, especially planetary bodies. Most recently he has been involved with NASA's Jet Propulsion Laboratory to include several sensor arrays on the next Mars Lander for performing chemical analysis of the Martian soil.

Gregory M. Kuhlman: Greg received a B.S. degree in Bacteriology from the University of Wisconsin-Madison in 1995. Following graduation Greg has worked for the University of Wisconsin-Madison, Covance Laboratories Incorporated, and Amgen Incorporated before coming to the Jet Propulsion Laboratory (JPL) in 2000. Greg's skills include



classical bacteriology techniques, modern molecular

biology techniques and extensive protein chemistry skills. Greg has mastered most modern chromatographic techniques such as High Pressure Liquid Chromatography (HPLC), Fast Protein Liquid Chromatography (FPLC) and Capillary Zone Electrophoresis (CZE). As an undergraduate at the University of Wisconsin-Madison Greg worked in the lab of Dr. Eric Johnson, world renown researcher of *clostridium botulinum* and other food borne pathogens, and has acquired the skills for working with pathogenic microorganisms. At JPL Greg focuses his time between two groups. He works with the Planetary Protection Technologies Group where he is researching and evaluating advanced technologies for molecular detection of microbes on spacecraft materials and in spacecraft assembly facilities. Greg also works with the Microdevices Laboratory where he is utilizing his biology skill set to test and study the effects of biofilms on space flight hardware.